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Catalytic conversion of biodiesel derived raw glycerol to value added products

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ABSTRACT

The huge amount of glycerol obtained during the production of biofuels has led to the search of alternatives for the use of this by-product. New applications for this polyol as a low-cost raw material need to be developed and existing ones need to be expanded. To address this problem, production of value-added molecules from crude glycerol is an effective alternative method for its disposal by incineration. Thus, the ready bioavailability, renewability and unique structure of glycerol make it a particularly attractive starting point for the production of a large number of specialty chemicals. The main purpose of this review is to focus on the catalytic reactivity of different kinds of catalysts in oxidation, dehydration, acetylation, etherification, esterification, acetalization, and ammoxidation process of glycerol conversion. Typical products are citric acid, lactic acid, 1,3-dihydroxyacetone, 1,3-propanediol, dichloro-2-propanol, acrolein, hydrogen, and ethanol. Recent studies on the catalysts, reaction conditions and possible pathways are primarily discussed.

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Contents

1. Introduction

The traditional applications of glycerol are as additives in food, tobacco, and pharmaceuticals. Alkidic resins and polyurethanes are vital towards the application of glycerol, as they are all utilized as feedstock for the production added-value compounds, such as bio-plastic, platform chemicals, and fuels (Table 1). However, for glycerol to be incorporated into consumer products, it must be refined and purified. The main approach of green chemistry is the provision of simplified refiniring and catalyst, while removing the need for purification through extraction [1]. Catalysts are tailored by controlling the size, spatial distribution, surface composition, thermal/chemical stability, shape, and electronic structure to reach the maximum selectivity on the glycerol conversion process (Fig. 1). Metal, metal oxides, and metal sulfides are the first batch of catalysts developed for hydrocarbon-based conversion that included partial oxidation and combustion reactions (Table 2). The development of highly porous, large surface area, heavily hydroxylated, functionalized, and pore

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Table 1
List of glycerol applications based on its natural characteristics.

Applications	Glycerol characteristics
Food industries • Humectant • Solvent • Antioxidant • Sweetener • Preserve Food • Filler • Thickening agent • Sugar substitute	i. It does not feed the bacteria that form plaques and cause dental cavities ii. Recognized as safe by the Federal Drug Administration and the U.S. food (FDA) iii. Considered as carbohydrate iv. Transesterified with alcohol to produce methyl (alkyl) ester
Medical, pharmaceutical and personal care • Allergen immunotherapies • Cough sirups • Toothpaste • Mounthwashers • Skin care • Expectorants and elixirs • Products • Hair care • Table holding agents • Fiber softener	i. Smoothness ii. Provide lubricant iii. Moisturizing properties iv. Allowed as feed additive v. Can cause a rapid, temporary decrease in the internal pressure vi. Hydrolyzed or saponified to produce fatty acids vii. Saponification with olive oil produces a sweet tasting substance
Botanical extracts • Tannins prevention • Alcohol free alternatives • Removal of numerous constituents and complex compounds • Preserving agent • Cryoprotective agent for microorganisms	i. Low glycemic load ii. Slowly absorbed by the body iii. High degree of extractive versatility iv. Good intrinsic property v. High extractive power assumes vi. Does not allow an inverting/reduction–oxidation of a finished extract's constituent vii. Bacteriostatic in its action
Antifreeze • Automotive applications • Enzymatic reagents • Acryoprotectant (for bacteria, nematodes, mammalian embryos)	i. Nonionic kosmotrope ii. Able to form strong hydrogen bonds with H_2O molecules iii. Able to disrupt the crystal lattice formation of ice iv. Freezing point $= -37.8$ °C (70% glycerol in water) v. Non-toxic vi. Formation of ice-crystals in the cell vii. Maintaining stability and vitality of the cell wall during the freezing process
Chemical intermediates • Nitroglycerin (ingredient of various explosives) • Soap making (glycerin) • Synthesis of resin and ester • Sub-lingual tablets • Ally iodide (blocks polymer, preservatives, organometallic, catalysts and Pharmecuticals)	i. Ethylene glycol functional groups ii. Non-toxic
Waste water treatment • Denitrification	i. Abundant carbon content ii. Porosity iii. Absorption ability

diameters ranging from microporous-to-macroporous supported catalyst is intended to reduce the costs of large-scale applications [1].

2. Catalytic oxidation of glycerol

Green technology, entailing hydrothermal electrolytic decomposition of glycerol using continuous flow reactor and equipped with metallic catalysts, has been developed. This overcomes the technical barrier brought about by the oxidation of glycerol, which is the selective catalytic oxidation engineering that operates on a polyfunctional molecule and a simple oxidant [2]. The derived oxygenated products from glycerol include dihydroxyace-

tone, hydroxypyruvic acid, glyceric acid, tartaric acid, oxalic acid, mesoxalic acid, and intermediates (e.g.: glyoxylic acid, glyceraldehyde and glycolic acid) (Fig. 2 and Table 3). The most studied metallic catalysts are Pd, Pt, and Au, although the main disadvantage of Pt and Pd is their deactivation at high reaction times [3]. To overcome this probl;em, support materials are incorporated into the metal catalysts to produce a hybrid system. A major product of glycerol oxidation within Pt/C or Pd/C catalyst is glyceric acid, with a selectivity of up to 70% (Table 4).

The selectivity on the oxidation process of the secondary OH group of glycerol was significantly improved by combining Pt with other metals, such as Bi, resulting in a yield of 30% hydroxyacetone at a 60% conversion rate. Pt/C combined with Bi has been
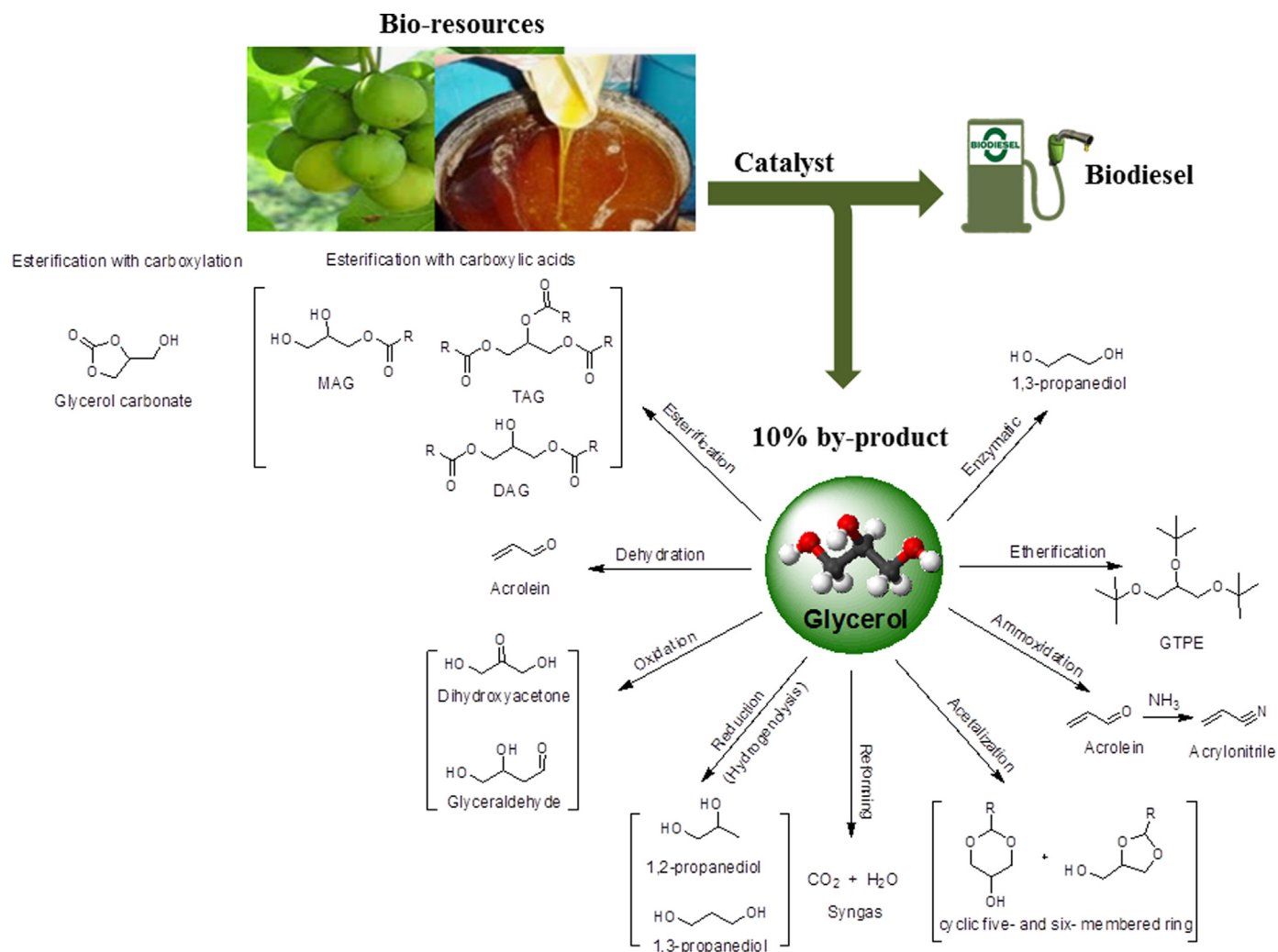
Fig. 1. Conversion of glycerol to value added chemicals: in general.

Table 2
Series of glycerol conversion with heterogeneous catalyst.

Catalysis used in glycerol production	Composition of products
Methanol	Glycerol: 38–96% Methanol: 14% Ash: 29%
Sodium methoxide	Glycerol: 30% Methanol: 13% Soap: 13% Moisture: 20% Salt: 2–3%
Alkali/lipase	Glycerol: 95–93% Salt: 5–7%

extensively studied, as it resulted in the oxidation of the primary and secondary OH groups of glycerol, which induce the production of tartonic acid up to 83 wt% on selectivity and 90 wt% of glycerol conversion at a pH of 9–11. Moreover, metallosilicates were also found to provide selective oxidation to glyceraldehydes, dihydroxyacetone, and glyceric acid via changes in pore sizes [4]. The dihydroxyacetone with Pt–Bi bimetallic catalyst in a semi-batch reactor was studied, and it was discovered that at 80 °C, pH 2, and 0.2 MPa, 48% and 80% selectivity and conversion of glycerol are achieved, respectively. However, the fixed bed reactor reduces the degree of conversion and selectivity by up to 5%, even when the

process parameters were similar. At a pH 11 and 50 °C, Pt/C yields glyceric acid with a selectivity of up to 70%. Electrochemical oxidation methods with Pt and Au modified with Pt–Pd and Ru nanoparticles have been also reported, demonstrating positive results in the oxidation of glycerol. Doping Pt/C catalyst with Bi provides the best selectivity to dihydroxyacetone by changing the direction of the reaction pathway towards secondary alcoholic groups [5]. The selective liquid-phase oxidation route to produce hydroxypyruvic acid over Bi-modified Pt catalyst has been reported in air-terminal oxidants [6].

Numerous studies showed that support materials that control oxidation selectivity are related to the nature of the catalysts and the reaction parameters. CeO_2-supported platinum catalyzes the oxidation of both primary OH groups, resulting in tartronic acid with a 40% yield [7]. Supported Au-catalyst resulted in a 90% selectivity of glyceric acid at a 100% conversion rate. Bimetallic catalyst composed of Pd, Au, and Pt supported on carbon resulted in a greater monometallic catalyst, due to the synergistic effect between the metals [6]. The oxidation on primary OH groups of glycerol was successfully catalyzed by carbon-supported Au, with a 100% conversion and 95% selectivity of sodium glycerate [8]. The selectivity of 1,3-dihydroxylacetone ranged from 10% to 80% of glycerol conversion of 80%, under the oxidation of aqueous glycerol solution over charcoal-supported Pt within pH 2–3, with the incorporation of Bi and Pt [4]. Furthermore, under mild conditions (60 °C, 3 h, H_2O as solvent), 1% of Au-supported
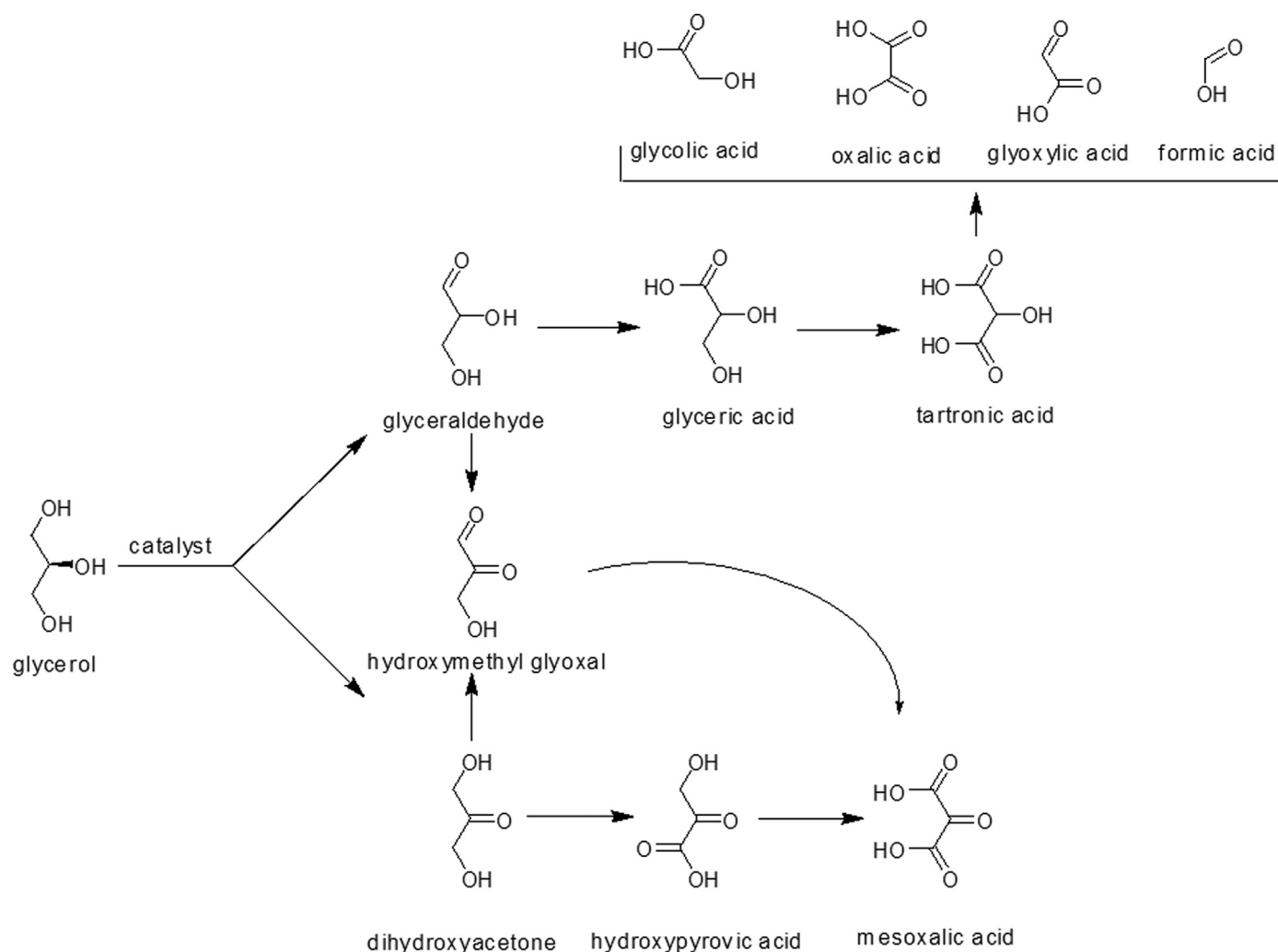
Fig. 2. Main reaction products of glycerol oxidation.

Table 3
List of derivatives derived from oxidation of glycerol and its applications.

Glycerol derivatives	Applications
Dihydroxyacetone	Synthon in organic chemistry, starting material in D, L-serin synthesis, tanning agent in cosmetics
Hydroxypyruvic acid	Flavor components, starting material in D, L-serin synthesis
Mesoxalic acid	Complexing agent, precursor in organic synthesis, anti-HIV agents
Oxalic acid	Cleaning or bleaching, removal of dust, mordant in dyeing processes, baking powder
Tartonic acid	Oxygen scavenger
Glycolic acid	Chemical peels performed by a dermatologist, skin care products

Table 4
Comparative on glyceric acid production with different heterogeneous support catalysts.

Heterogeneous catalyst	Selectivity of glyceric acid (wt%)	References
Pd/activated charcoal	30	[4]
Pt/activated charcoal	55	[5]
Bi/activated charcoal	77	[6]

charcoal, or 1% Au-supported graphite, resulted in a 100% selectivity towards glyceric acid [9]. This is similar with Pt/C and Pd/C, where the selectivity of glyceric acid reached 55% and 77%, respectively, with a 90% glycerol conversion [10]. This prevents the product from over-oxidation, which avoids the degradation of

products until total oxidation to CO_2, where the promoter favors secondary alcohol oxidation. However, in the absence of a promoter and with the presence of a Pt–Bi bimetallic catalyst, the primary alcohol is oxidized to COOH, and produces a series of intermediates (dihydroxyacetone, hydroxypyruvie acid, oxalic acid, tartaric acid, mesoxalic acid, glyceric acid, glyceraldehyde, glycolic acid, and glyoxylic acids). Thus, researchers focused on mono/bimetallic catalyst of Pd, Pt, and Au, using O_2 as an oxidizing agent. Pd and Au are more selective towards glyceric acid under basic conditions compared to Pt [11]. The production of intermediates is dependent on the pH of the reaction. The glyceraldehyde and tartaric acid are obtained at basic pH, while hydroxypyruvic acid was obtained under mildly acidic pH, and dihydroxyacetone and hydroxypyruvic acid were obtained under strongly acidic pH. In acidic conditions, secondary alcoholic groups,
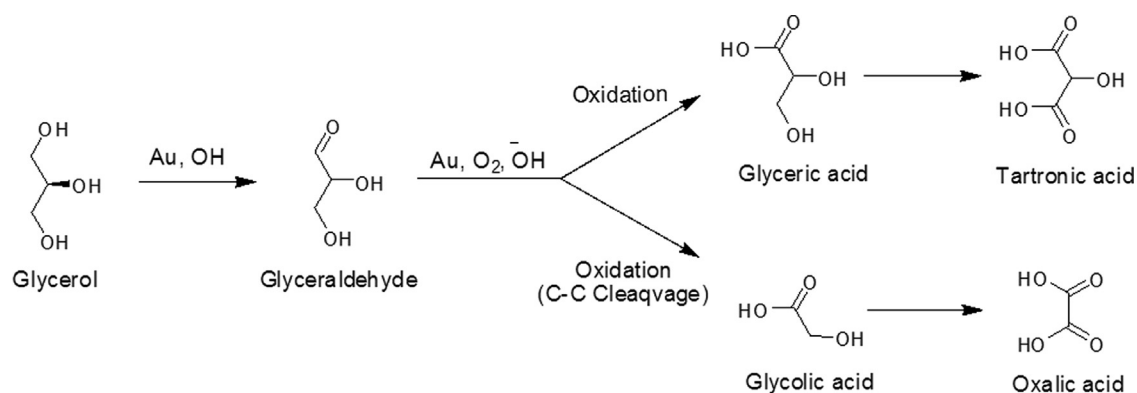
Fig. 3. Reaction pathway for glycerol oxidation using supported Au catalysts.

hydroxypyruvic acid, and dihydroxyacetone were produced, while at basic conditions, the primary alcoholic groups are favored for oxidation, which result in the production of glyceric acid. Thus, under similar process parameters, 70% and 35% on the selectivity of glyceraldehyde and hydroxypyruvic acid were obtained, respectively. Pt–Bi bimetallic catalyst obtained 83%, 74%, 37%, and 39% selectivities for tartaric acid, hydroxypyruvic acid, dihydroxyacetone, and mesoxalic acid, respectively. The redox process with Pd/C showed a 5% higher selectivity compared to a Pt–catalyst [12]. The selectivity increased with particle diameters that were diminished due to Au-catalyst (Fig. 3).

Carbon nanoparticles were shown to be the most chemically active support material, and confirmed the relationship between selectivity with total glyceraldehyde yield and particle size [13]. The application of Au–Pd bimetallic catalyst with the greatest turnover frequency found on Au-mono metallic catalysts and maximum selectivity for glyceraldehyde was obtained by the incorporation of Pd, while the selectivity of the conversion was more related to the quantity of Au. Bimetallic catalyst of Au–Pd/C resulted in low temperature reactions, with a 50% conversion rate [14]. Glycerol oxidation on metal oxide resulted in (2,2-dimethyl-1,3-dioxolan-4-yl) methyl acetate, glyceric, glycolic, dihydroxyacetone, tartronic and oxalic acids derivative compounds [15]. The fuel additive is produced via the oxidation of glycerol, and is commonly used as a biodiesel additive. The optimum condition for the production of (2,2-dimethyl-1,3-dioxolan-4-yl) methyl acetate is achieved at various conditions (e.g.: amount of feeding glycerol, oxidation rates). Glycerol is stable under high pressure aqueous state and high temperature conditions during hydrothermal treatment with catalysts [16]. The use of bimetallic catalyst produced glycoaldehyde and glycolaldehyde, formic acid, and lactic acid as major products, with a low formation of H_2, glyceraldehyde, glycolic, and acetic acids. Au–Pt/TiO$_2$ catalyst and O$_2$ in glycerol conversion to lactic acid are used as reaction parameters of 90 °C with NaOH:glycerol ratio of 4:1 to reduce the reaction temperature while achieving higher glycerol conversion rates [17]. The remaining steps from glyceraldehyde to lactic acid require alkaline conditions, or further oxidation would take place, resulting in the conversion of glycerol into glyceric acid. The reaction reached high glycerol conversion rates (> 100%) and lactic acid selectivity (85%) at lower temperatures, with a glycerol concentration of 0.22 M. Once, the concentration of feed glycerol increased to 2.5–3.5 M, it consequently, increased the selectivity of lactic acid to 89.9% [17]. It is noted that some of the super-solid base catalyst sincluded compounds such as CaO, Al$_2$O$_3$, NaOH, and Na that are not suitable to promote the production of lactic acid, due to corrosion, low reactor productivity, and restricted solubility in H$_2$O [18]. The highest yield on the production of lactic acid was recorded at 40.8 mol% selectivity, at a 97.8% conversion rate with

CaO catalyst at 290 °C and 150 min [19]. High H$_2$O content in the reactant would affect the total yield of lactic acid. The solid basis tends to interact with H$_2$O and decrease its catalytic activity. NaOH is a good catalyst for lactic acid production, with a 100% conversion of glycerol, but the high initial concentration of NaOH corrodes the stainless steel reactor [19]. Bronsted acids (e.g.: Na$_2$O, K$_2$O, MgO and BaO) are unsuitable for the production of lactic acid [20], due to its strong interaction with O$_2$ ions, rendering it vulnerable to CO$_2$ and H$_2$O contaminations, although it does make its utilization in aqueous media viable. Supported Pt–Bi catalysts (5 wt% Pt, 5.4 wt% Bi) on active charcoal are employed in continuous flow experiments (120 °C, 1 bar O$_2$) using the trickle bed reactor up to 50% selectivity of dihydroxyacetone [21]. Monometallic/Au nanoparticles on carbon and TiO$_2$ have recently been reported in the continuous flow oxidation of glycerol, at a temperature of 60 °C and 11 bar of O$_2$ pressure [22]. CaO is extensively used to catalyze the glycerol conversion for lactic acid production. At parameters of 290 °C and 15 min, with a molar ratio of glycerol:CaO=0.7, 97.8 mol% and 40.8 mol% are achieved on the conversion and selectivity of glycerol with high lactic acid production (3.35 g min^{-1} L^{-1}). Na$_2$(SiO$_2$)$_n$O catalyst was proven effective, with high selectivity of lactic acid production (90.7%) at 300 °C and 90 min [23]. The lactic acid production from glycerol with NaOH catalyst parameters of 300 °C, 220 min, and 1.1 M glycerol reached 80.5 mol%, with 92.8% glycerol conversion [24]. The presence of Cu and/or Cu$_2$O-based catalyst decreased the reaction temperature to 240 °C on glycerol conversion to lactic acid with an NaOH catalyst.

3. Catalytic dehydration of glycerol

Dehydration of glycerol is not easy, since the C=C bond is thermodynamically more favorable than the C=O bond (free reaction enthalpy by 35 kJ mol^{-1} less) (Fig. 4).

The C=C bond is kinetically more active than C=O bonds, and the boiling point of glycerol is 290 °C, whereby the catalytic glycerol dehydration normally requires a heating temperature of 250–350 °C. Thus, the catalyst deactivation occurring during the dehydration process is due to the formation of glycerol by-product, coke deposition, and acrolein. Thus, the ideal glycerol dehydration is thought to occur in solid (180–340 °C) and liquid (250–340 °C) phases. Heterogeneous catalysts (e.g.: H$_3$PO$_4$/Al$_2$O$_3$ or H$_3$PO$_4$/TiO$_2$) are normal catalysts used for solid phase conversion, while the liquid phase catalysts such as mordenite, montmorillonite, acidic zeolite, oxide, mixed oxide, and heteroplyacid are more predominant [25]. The life-time of the catalyst was improved by using diluted glycerol compared to pure glycerol. Furthermore, the selectivity of glycerol dehydration in the acrolein production is

optimized with sufficient temperature and partial vacuum conditions. The reaction catalyzed by acids occurred either in gas or liquid phase. 66.8% of acrolein yield and 84% of the glycerol conversion were achieved at 260 °C, with 0.85 bar and H_3PO_4/C catalyst [26]. 70% of the total yield of acrolein achieved with Hammett acidity constant was between -10 and -16. At lower acidity conditions, the acrolein yield was 60%, and the catalyst was comparatively deactivated [27]. The reaction was mostly accompanied by side reactions, resulting in acetaldehyde, hydroxypropanone, propanaldehyde, adducts, acetone, and polyaromatic compounds, which consequently form a coke on the catalyst. The byproducts series of acrolein, like hydroxypropane and propanoldehyde, and isolate necessitate the purification and separation steps, which result in higher recovery costs. Furthermore, solid acid catalyst ZSM-5 zeolite was used to enhance the product separation, maintain catalyst regeneration over large time periods, and induce availability for wide range of glycerol concentrations without co-solvent, polluted feeds, and byproducts [28].

Due to its crystalline nature composed of SiO_4 and $[AlO_4]^-$ tetrahedra, constant electroneutrality, cation characteristics of $[AlO_4]^-$, highly acidic charge compensation, multi-dimensional microporosity, shape selectivity, and valorization of hydrocarbon streams in refineries, zeolites are one of the promising catalysts in glycerol dehydration. With zeolites, glycerol dehydration at 330–360 °C reached 100% glycerol conversion, with an acrolein selectivity of more than 70%. The selectivity significantly increases with reaction temperature at 83% and 500 °C without significant coke formation [29]. There was good interaction between secondary OH groups of glycerol and zeolite, resulting in acrolein being selectively formed. Zeolite catalyst is used in the glycerol dehydration for light olefins production. To enhance the acid sites for glycerol dehydration, zeolites were impregnated with metals [28]. The metal was responsible for the physical changes such as the micropore area, surface area, and pore volume of the synthesized catalyst, which resulted in 16.3% of light olefin selectivity [30]. The acrolein selectivity found on zeolite is considered to be lower than other catalysts due to the higher acidity of zeolites. Application of other heterogeneous catalyst and super critical H_2O as a reaction medium for the conversion of glycerol to acrolein garnered some interest among the scientific community (Table 5).

The support material incorporation is documented to increase the selectivity and conversion of the glycerol dehydration. 75% on selectivity and 100% on conversion of glycerol to acrolein were observed with Al_2O_3 and SiO_2/Al_2O_3 supports for the silicotungstic acid catalyst, respectively [36]. TiO_2 and SiO_2 have also been used for H_2SO_4, H_3PO_4, and $H_3Mo_{12}O_{40}P$ support, with almost 58 mol% conversion of acrolein to allyl alcohol at 300–320 °C [37]. Acrolein was produced with mixed oxide (e.g.: Bi–Mo and Nb_2O_5) catalyst under gas phase oxidation. There is some effort to synthesize $ZrO_2–FeO_x$ mixed oxide catalyst and study its performance towards the production of allyl alcohol derived from glycerol [38]. The production of allyl alcohol and propylene initially involved the R-COOH from acetol production, followed by their ketonization. The $ZrO_2–FeO_x$ components are highly resistant to glycerol conversion from both mixed metal oxide and alkaline metal [38]. Conversion into acrolein is more convenient at lower temperatures, while at high temperatures, they are only suitable for conversion into acetaldehyde. High selectivity (75%) for acrolein from oxidation of glycerol at 275 °C was attained with $[Si_n+W_{12}O_{40}]^{8-n} \cdot xH_2O$ catalyst [39]. Meanwhile, a series of $VOPO_4$, including $VOPO_4 \cdot 2H_2O$, $VOHPO_4 \cdot \frac{1}{2}H_2O$, and $(VO)_2P_2O_7$, demonstrated good catalytic activity. $VOHPO_4 \cdot \frac{1}{2}H_2O$ gives 66% acrolein at 100% glycerol conversion [40]. The performance of $(VO)_2P_2O_7$ is strongly dependent on the activation temperature, and catalysts calcined at 800 °C resulted in the selectivity of useful products at 95% and 100% conversion rates.

The double glycerol dehydration was achieved under sub- and supercritical H_2O media at lower pressure. This is effective in eliminating volatile products from the catalyst, and extends its service life [41]. The glycerol decomposition in supercritical H_2O without the addition of catalysts was recorded at 349–475 °C, pressures of 250, 350, or 450 bar under a reaction time of 32–165 s, with different derivative compounds [42]. The reaction continued in a tubular reactor with varying parameters and derivative products (e.g. formaldehyde, allylic alcohol, propionaldehyde, acetaldehyde and acrolein). The maximum acrolein yield was recorded at 27%, with a selectivity of more than 38% at parameters of 356 °C, 450 bar, and 50 s [42]. The reactions enhanced the catalyst's selectivity of glycerol to acrolein, since high initial glycerol content resulted in glycerol polymerization, and allowed for degradation under the corrosion of catalyst. Thus, the influence of acid catalyst on the selectivity of dehydration reaction of glycerol to acrolein under supercritical H_2O in the presence of H_2SO_4 catalyst is recently being studied. Acrolein production has a linear relationship with the amount of glycerol feeds and the concentration of H_2SO_4 [43]. Optimized results afford acrolein to up to 74% yield under the reaction conditions of 400 °C, 345 bar, and 12 s. The rate constant of glycerol decomposition was recorded to be greater than without H_2SO_4 catalyst, with 72% on acrolein selectivity (Table 6).

Another glycerol dehydration is implemented with liquid raw glycerol, directly added into fluidized bed reactor, vaporized, and reacted to generate acrolein over W-doped Zr catalyst [46]. This results in minimum salt accumulation and the abandonment of salt crystals, which are loosely bound to the surface, requiring mechanical agitation to be separated from the catalysts. In order to
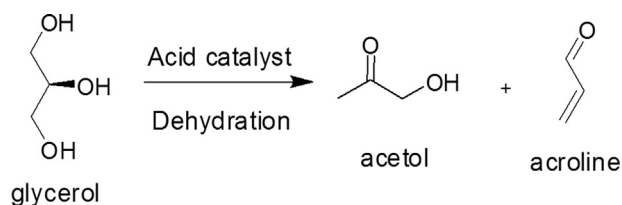

Fig. 4. Continuous flow glycerol dehydration to acrolein.

Table 5
List of heterogeneous catalysts used in different dehydration parameters of glycerol.

Heterogeneous catalyst	Process parameters		Conversion of glycerol (%)	Selectivity of acrolein (mol%)	References
	Temperature (°C)	Pressure (MPa)			
Zinc sulfate	360	25	50	75	[31]
Sulfuric acid	400	34.5	90	80	[32]
Silicotungstic acid	275	101	100	80	[33]
Zeolite	350	101	100	100	[34]
Phosphoric acid/activated carbon	260	0.85	85	67	[35]
Tungsten oxide/titanium oxide	300	25	100	85	[63]

overcome this problem, ZnS_2 was used as electrolytes, with 38% acrolein yield, and almost 75 mol% selectivity being produced at parameters of 360 °C, 250 bar, and 60 s. ZnS_2 electrolyte reduced the pressure of the reaction [47]. Glycerol catalyzed was dehydrated with metal oxide catalyst (e.g.: Al, V, Sb and Nb oxides) before being grafted with $R-NH_3$ to form C–N bond. The glycerol conversion process was done to propandiole via a combination of dehydration and hydrogenation. The process was initiated with glycerol dehydration to acetol with acid catalyst, followed by acetol hydrogenation to propandiole with metal catalysts.

4. Catalytic acetylation of glycerol

The catalytic acetylation of glycerol is a path to enhance the profitability of biodiesel products of acetins (mono-, di- and tri-esters of glycerol). These series of acetins are mainly used as transport fuel additives (Table 7). Mineral acid catalyst is commonly used to catalyze the glycerol acetylation process. However, mineral acid catalyst induced environmental problems, such as excessive catalyst usage, toxicity, no recycle-ability, and serious corrosion of equipment. Therefore, solid acid catalysts (e.g.: zeolites, amberlyst, sulfonic acid functionalized mesostructured materials, montmorillonite, niobic acid, heteropolyacids), and metal oxide catalyst are present in the glycerol acetylation process [48]. A series of zirconia heterogeneous catalysts, such as $ZrO_2/SiO_2/ME$, $ZrO_2/SiO_2/SG$, $HClSO_3/ZrO_2$, and $S-ZrO_2$ towards the acetylation of glycerol, have been recently reported. It was found that $HClSO_3/ZrO_2$ exhibits the highest catalytic activity, with 100% selectivity in action, followed by S/ZrO_2 (91%) and H_2SO_4/ZrO_2 (50%) [49]. The acetylation reaction catalyzed with $ZrO_2/SiO_2/ME$ and $ZrO_2/SiO_2/SG$ exhibits the lowest selectivity, with 29% and 27%, respectively. Thus, acetylation could be catalyzed by not only Bronsted acid sites, but also Lewis acid sites, thus, sulfated ZrO_2

Table 6
Different heterogeneous catalysts on the selectivity of acrolein from the dehydration process of glycerol.

Heterogeneous catalyst	Selectivity (%)	References
WO_3/ZrO_2	75	[44]
Zeolite	75	[45]
Zeolite	67	[46]

Table 7
Acetylene derivatives of acetylation of glycerol and its industrial applications.

Acetylene derivatives	Industrial applications
Triacetin	• Antiknock additives for gasoline • Improve the cold and viscosity properties of biodiesel • Production of photographic films • Perfumery industry
Diacetin	• Solvent for various dyes • Softening agents • Printing ink • Plasticizer
Monoacetine	• Manufacture of dynamite • Tanning leather • Cryogenics • Raw materials for production of biodegradable polyester • Food additives • Explosive and smokeless powder

catalyst is indicative of higher activity than non-sulfated ones. This is due to the diversity of acid sites' amount, acid strength, and the robustness of the properties of the catalyst. However, the usage of ZrO_2 based catalyst reports some drawbacks, such as high pressure of the reaction, high diffusivity, acid site deactivation, and high molar ratios of acetic acid to glycerol. Therefore, ion exchange resins, such as Amberlyst 15, Abmbertlyst 36, Dowex 50Wx2, Domex 50Wx4, and Dowex 50Wx8, were used as catalysts, and 100% selectivity of triacetin was achieved at high molar ratio (acetic acid:glycerol 24:1) and high pressure (200 bar) [50]. It was determined that the best performance for 6.25 g of catalysts was exhibited by Dowex 2 and Amberlyst 36. The catalytic performance of the resins was unaltered after washing with distilled water, indicating that sulfonic species were not removed by leaching, making it convenient for recycling and reusing for up to 5 cycles. However, such high molar ratio and ineffectiveness in a non-polar media, desulfonation due to high working conditions, deactive by metal ions/cations, the difficulty of the separation of unreacted reactant and sub-products render the application of resin catalyst unfeasible on an industrial scale [48]. Heterogeneous catalyst also suffers from poor thermal stability, high solubility in polar media, poor regeneration ability, and low specific surface areas. Supported materials, such as silica or activated carbon, were then applied to increase the surface area of the catalyst, even though the accessibility and efficiency of the catalyst are reduced concurrently. Alkylated sulfonic acid (propyl-, arene-, and perfluoro-sulfonic acid), supported by siliceous mesoporous, causes the formation of di and tri-acetin to linearly increase with the acid strength, while mass transport property was concomitantly offered by mesoporous as the support material [51]. In the case of niobic acid, supported with heteropoly tungstate with Keggin structure, compels the acetylation activity to occur within a short reaction time (30 min), with 90% of glycerol conversion. A new catalytic acetylation process, based on metal oxide (e.g.: CeO_2/ZrO_2, CeO_2/Al_2O_3, SO_4^{2-}/CeO_2 and $SO_4^{2-}/CeO_2-Al_2O_3$), was introduced due to its stability, low costs, regenerability, and being 100% active over a wide range of reaction parameters, and 100% on the conversion of glycerol, with 90% selectivity of triacetin.

5. Catalytic esterification of glycerol

The esterification of glycerol was carried out with basic, acid, multi-valet metal salt, resins, zeolite, heteropolyacids, and sulfonic acid as the heterogeneous catalyst (Fig. 5). The catalysts used in basic catalysis were the alkali metal hydroxides (NaOH, KOH) and metal alkoxides ($NaOCH_3$, $KOCH_3$), and a combination of both hydroxides and alkali metal alkoxides (alkaline catalysts). They are also eligible for other alkoxides butoxides and propoxidos catalysts. The heterogeneous acids being used include H_2SO_4, RSO_2OH, $PO(OH)_3$, or HCl, among others [52]. Synthesis of monoglyceride by the esterification of glycerol with oleic and lauric acids with functionalized ordered mesoporous materials containing $R-SO_3H$ groups as a catalyst and its effect on alkyl chain length of $HSO_3-R-MCM-41$ on the esterification with fatty acid were studied. The distance between $R-SO_3H$ groups and its porosity balanced the nature of its organic groups [53]. There is some interest in conducting the production process of monoglycerides in alkaline catalyst under a nitrogen atmosphere, or aluminum and zirconium-containing mesoporous molecular sieves in supercritical carbon dioxide medium. High glycerol conversion with a great selectivity to three esters of monoglycerides was achieved. Esterification of glycerol has also been conducted with acid catalysts, such as dodecamolyb-dphosphoric acid engaged in the zeolite, tungstophosphoric acid supported on silica/activated carbon, niobic acid supported ZrO_2, sulfonic acid groups linked to mesostructured materials,
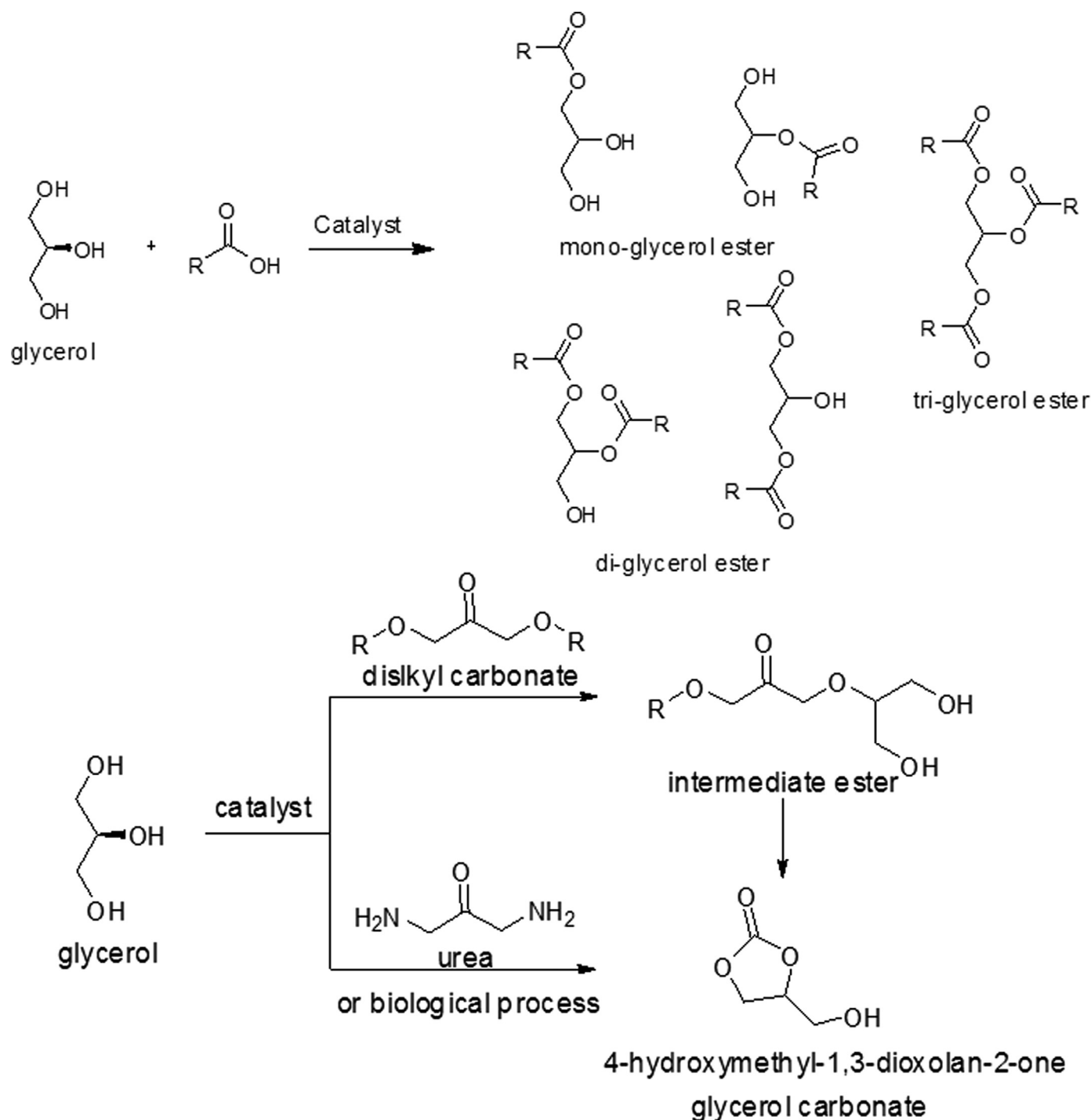
Fig. 5. Main reaction products in the esterification of glycerol.

and activated carbon treated with H_2SO_4 [54]. Esterification of glycerol, with a series of multi-valet metal salts, was conducted in the production of mono- to dilaurins, and it was discovered that chloride-based catalysts, such as $ZrOCl_2 \cdot 8H_2O$, and $AlCl_3 \cdot 6H_2O$, are the most active in the formation of the monolaurin. In the case of dilaurin, sulfate-based catalysts, such as $Fe_2(SO_4)_n \cdot H_2O$ and $Zr(SO_4) \cdot H_2O$, are indicative of the most convenient and selective esterification process [55]. The use of basic catalysts allows the obtainment of reaction rates of almost triple than those obtained with the same amount of catalysts in acidic conditions. The production of glycerol acetate is one of the examples under esterification of glycerol with resin catalyst; Amberlyst resin [56]. As strong acid ion exchange

resin, Amberlyst resin expects two large-pore zeolites H-Y and H-Beta to be used as catalysts in the etherification of glycerol with isobutylene or tertbutyl alcohol. The continuous flow synthesis of glycerol acetate was documented under supercritical CO_2 conditions (110 °C, 200 bar, 120 min, CO_2 flow: 0.2 mL mn^{-1}) using the acetic acid presence of Amberlyst 15 catalyst. The ratio of glycerol to Aberlyst 15 was speculated to play a major role as opposed to other insignificant contributions (e.g.: pressure, time, CO_2 flow rate). The stability of Amberlyst 15 under those kinds of harsh conditions is not commented, particularly after reuse, structure, acidity, and surface properties. Comparatively, the catalytic synthesis of glycerol mono-acetate was reported using a continuous bed column reactor (50 °C,

30 min) packed with Amberlyst 16 (5 g) catalyst with a good selectivity of corresponding monoacetate [57]. Amberlyst 35 is a catalyst for glycerol esterification, with 65% selectivity and almost 100% glycerol conversion. Biocatalyst (e.g.: Novozyme 435 lipase) production of acetate-base has also been highlighted. Starting from ethyl acetate and vinyl acetate as acyl donors, the selectivity towards acetins was found to be related to the residences' time and temperature. However, both parameters insignificantly affect the distribution of mono-, di, and tri-acetin. The production of mono-acetin strongly depends on the flow rate. The use of vinyl acetate at retention time significantly produced diacetin as a main reaction product, with high conversions and selectivities, brought about by the acyl donor of the vinyl acetate. 84% of the production of triacetin is obtained at low flow rates of 0.5 ml min^{-1} and retention time of 4.8 min at 60 °C, with only minor quantities of diacetins [58]. However, the diacetin production increased by 70% at a retention time of 28 min.

6. Catalytic reforming of glycerol

H_2 or syngas raw glycerol was confirmed to be a practical alternative for producing H_2 or syngas via gasification technique (Fig. 6). In-situ TGA analysis showed that the thermal decomposition mechanism of raw glycerol involved the degradation phase of CO_2, H_2, CH_4, and CO as major gas products. The optimal conditions for H_2 production of glycerol at 600–700 °C, and H_2O/glycerol ratio of 9–12 at atmospheric pressure produced 6.2 mol of H_2 per mole of glycerol. The CH_4 production was minimized, while the formation of carbon is thermodynamically inhibited [59]. Supercritical H_2O is another gasification technique in the production of H_2, with NaOH being commonly used as catalyst [60]. The high selectivity of H_2 production with no char was obtained (up to 90 vol%). Reaction by protons or OH groups derived from alkali catalyst can be performed under supercritical conditions. H_2O acted as solvents and catalyst due to the self-dissociation, which are taken for the formation of hydroxyl ions and protons. Thus, the conversion of glycerol with super critical H_2O can be considered to occur with two consequential steps. Initially, the ionic reactions would occur at high pressure and/or high temperature, followed by a degradation reaction of free radicals at low pressure and/or high temperature. The reaction rate significantly increased with an increment of temperature, until the critical temperature is obtained; then it is consequently reduced to subcritical levels [61].

The quantity of inorganic alkaline catalyst in the raw glycerol affected the concentration of H_2 being produced, reported to be 2.7 wt% on NaOH, producing 42 vol% of H_2. The long chain fatty acids are hardly reformed, and are more likely to form carbon instead [62]. Therefore, methanol, acrolein, propionaldehyde, ethanol, allylic alcohol, formaldehyde, CO_2, CO, and H_2 products are obtained from these reactions. The production of acetaldehyde and formaldehyde is increased by pressure, indicating that both products are mainly formed by ionic reactions. Methanol and allylic alcohol formation is inversely related to pressure, indicating that these compounds are formed via free radicals. The free radical mechanism also occurs in the formation of gas products at high temperatures and low pressure. The production of 64.8 mol% H_2 from glycerol, ethylene glycol, and sorbitol at a temperature of

Fig. 6. Hydrogen generation via catalytic aqueous-phase reforming of glycerol.

227 °C under high pressure in a single-reactor aqueous-phase reforming process is assisted by Pt/Al_2O_3 [63]. The Sn-promoted Raney-Ni catalyst resulted in H_2 production by aqueous phase, reforming at a lower heating temperature of 227 °C and a pressure of 2.58–5.14 MPa [64]. The incorporation of Sn increased the H_2 production (66 mol%) with the decrease of the CO_2 production (32 mol%). The atomization of glycerol was assisted by the presence of Ni-catalyst in a superheated steam condition (60–80 °C). H_2 production went up to 77 wt%, and linearly increased with steam temperatures. However, the disadvantage of this type of H_2 production is that the CO being produced requires the purification of the H_2 steam in order to prevent fuel cell poisoning. This technique requires the use of large amount of O_2, which would increase the production of CO while reducing the H_2 yield. The reaction with low concentration of glycerol at high temperatures resulted in high CO_2 concentration, with most products remaining in the liquid phase [64]. To selectively produce syngas, inert materials, such as carbon-based materials, are preferred as a catalyst support instead of using metal oxide to increase the activation of water. The combination of chemical inertness is reported to prevent ionic-catalyzed polymerization reaction and hydrophobicity of reactions, consequently providing the stability of reactions in aqueous phase processing.

The H_2 production has taken place via the steam reforming process of glycerol at high temperature endothermic reactions. The viability of Pt/Al_2O_3 heterogeneous catalysts in the production of H_2 from glycerol, with optimum reformer performance, was achieved at 880 °C and at a flow rate of 0.12 mols min^{-1} per kg of catalyst [65]. The presence of Pt favors the cleavage of C–C bonds over C–O bonds, especially under gas-phase conversion (225–275 °C). Pt surface is predominantly covered by adsorbed CO molecules, which inhibit the performance of the catalysts. Pt/Al_2O_3 catalyst has been doped with La_2O_3 or CeO_2, and the addition of metal oxides to Pt/Al_2O_3 catalysts was found to considerably enhance the glycerol steam reforming, with high H_2 and CO_2 production due to the greater surface and distribution of Pt [66]. A better catalytic stability is obtained by the composition of $Pt/La_2O_3/Al_2O_3$ at working systems of 350 °C, while the $Pt/CeO_2/Al_2O_3$ catalyst strongly deactivates after 20 h under similar conditions. PtRu and PtRe have been identified as alloys that could offer the reforming activity of Pt, but one that binds CO less strongly, thus mitigating the inhibition of reactions in the presence of desired products [67]. Both these alloys were active in the production of syngas, from glycerol with less susceptibility, to adsorbing more CO. The production of syngas can be tuned by the modification of the introduced pressure and temperature; at lower pressure and temperature, the water gas is not equilibrated, thus the system produces more CO and H_2 gasses. Summary of Ni, Ce, and Ru heterogeneous catalyst supports is provided in Table 8. Glycerol aqueous reforming is one of the promising techniques to grant access on the production of relevant chemicals (e.g.: propanediols). The effect of various heterogeneous catalysts under different suitable conditions for the production of propanediol derived from glycerol is summarized in Table 9.

Some studies combined the dehydration and hydrogenation processes (hyrogenolysis process) of glycerol catalyzed with solid acid catalysts (sulfated zirconia, zeolites, ion exchange resin and tungstic acid). The conversion process starts with selectively transforming the middle OH groups of glycerol into a tosyloxyl group, before removing the transformed group via catalytic hydrogenolysis. The hydrogenolysis process generally involves three main steps: acetalization, tosylation, and detosyloxylation. The production of propanediol was performed at mild conditions (358 K; 5 MPa) of sulfolane with Ru catalysts [71]. The process is scarified on reaction activity, total yield, and degree of selectivity of propanediol. The combination of Ru/C with ion exchange resin indicated the highest activity, even under mild conditions
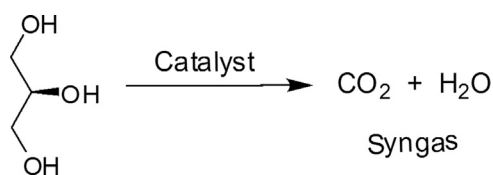
(temperature: 393 K; pressure: 5 MPa), rather than other solid acid catalysts mentioned above [72]. This encourages other studies to move forward in the application of Ru catalyst, with SiO_2 expecting the combination of Ru/SiO_2 of being an effective catalyst in the conversion of glycerol under H_2 conditions. This is normally developed in a continuous flow fixed-bed reactor (at temperature up to 235 °C, pressure of 31 bar), with the addition of ZnO and NiMo (in ratio of ZnO:NiMo 2:1) to catalyze the reforming reaction. The reactions are typically carried out over ZnO and/or NiMo catalyst, due to the ability of both heterogeneous catalysts in achieving the formation of C–O breaking reaction and forming a light hydrocarbon, rather than the C–C breaking reaction, which could lead to CO, H_2, and CO_2 production [73]. The co-catalyst, such as SiO_2, MgO, HZSM-5, TiO_2, Al_2O_3, CeO_2, and ZrO_2, reported that protocol provides better selectivities (53%) and reduces the reaction pressure. The synergistic effect between physically-mixed skeletal NiMo and ZnO would enhance the Lewis acidity of ZnO by chemisorbed CO_2 from the reforming process of glycerol to assist ZnO in promoting further dehydration of glycerol to acetol, as well as the NiMo-catalyzed hydrogenation of actual to 1,2-Propanediols. On the other hand, the production of 1,2-Propanediols via the hydrogenation of glycerol can be achieved using metabolically engineered microorganisms (e.g.: *Clostridium acetobutylicum*) [74]. The reduction of glycerol to 1,2-Propanediol was catalyzed with Co/MgO, and indicated a low conversion of glycerol (> 55%), with a selectivity as low as 42%. However, as Cu/Al_2O_3 is used as the catalyst, the glycerol conversion at 190–200 °C under 0.1 MPa partial H_2 pressure will reach 100%, with a selectivity of more than 75% [75]. Several supported mono- and bi-metallic transition metal catalysts (e.g.: Pt, Cu, Au, Au–Ru, Ni, Ru–Re and Cu–ZnO) were extensively used in the glycerol reforming process for the 1,3-Propanediols production. The activities on the series of the aforementioned catalyst are arranged in the following order: $Ru \approx Cu \approx Ni > Pt > Pd$ [76]. The conversion of glycerol to 1,3-Propanediols, an aqueous phase glycerol degradation protocol reportedly, uses a series of ternary catalyst system $Pt/WO_3/ZrO_2$

(at composition of 10 wt% Pt; 10 wt% WO_3; 80 wt% ZrO_2) in a fixed-bed continuous flow reactor (temperature of 130 °C, a pressure of 40 bars, 24 h), and managed to produce a 70% conversion of glycerol, with 32% yield and 46% selectivity of 1,3-Propanediols as its main products, with n-proponal and i-propanol being other major products and a selectivity of more than 50% [77]. This deoxygenation mechanism involved proton transfer and hydride transfer steps. One step reaction on conversion of glycerol to 1,3-Propanediol uses a direct chlorination of glycerol. High glycerol conversion (100% selectivity) at 90–110 °C is produced in a batch reactor system. This is improved by the support materials, such as ZnO, C, Al_2O_3, H_2O, Sulfolane, Dioxane, and H_2WO_4.

7. Catalytic reduction of glycerol

Several research works have used heterogeneous catalysts such as Zn, Cu, Mg, Co, Mo, Pd, Ni, and Pt to catalyze the reduction of glycerol. The main products of this reduction process could be ethyleneglycol, 1,2-propileneglycol, 1,3-propileneglycol, lactic acid, acetol, propanol, or even acrolein, with wide reaction parameters on temperature (200–350 °C) and pressure (2000–5000 psi). Cu is reported to produce the highest yield and selectivity on the production of propylene glycol, while low selectivity to ethylene glycol. Ru- and Pd-based catalysts resulted in low selectivities of propylene glycol, due to the competition in the hydrogenolysis process [78]. C–C and C–O bonds are being excised to produce lower alcohols and gases. Otherwise, undesirable products, such as ethylene glycol, or even CH_4, might be obtained. The degree of reduction is independent of the initial glycerol concentration, while it is strongly supported by catalyst types and reaction process to produce ethylene glycol and propyleneglycol with high yields and selectivity (Fig. 7).

The selectivity of ethylene glycol is not linearly connected with the pH of the reaction, with less production at low basic conditions. Hydrogenolysis of glycerol also occurred in the presence of bimetallic and bifunctional catalysts, such as PtRu/Ca and AuRU/Ca. Ru catalyst renders the conversion process to occur at mild conditions at a temperature of 180 °C, H_2 pressure of 5 MPa, and reaction time of 12 h, resulting in high selectivity of ethylene glycol (41%). Other researchers focused on glycerol concentration, pressure, temperature, and residence time, and found a significant relationship between the factors with the conversion and selectivity of ethylene glycol [79]. Other bimetallic systems for the reduction of glycerol are listed in Table 10.

8. Catalytic etherification of glycerol

Etherification process of glycerol produced a low polymerization (with lineal, branched or cyclic chains) and oxygenated compound known as polyglycerols (e.g.: glycerol tertiary butyl ether, methyl tertiary butyl ether, 1,3-ditertbutyl glycerol, 1,2-ditertbutyl glycerol and 1,2,3-tri-tertbutyl glycerol). It can be more

Table 8
Series of catalysts and their support for re-forming process of glycerol.

Heterogeneous catalyst	Support	Function of support
Ni	MgO	Increase stability of the catalyst under reaction conditions
	CeO_2	
	TiO_2	
	Al_2O_3	
	La	Increase hydrogen selectivity
	Ce	
	Mg	Increase surface catalyst concentration
	Zr	Improve capacity to activated stem
Ce	Ir	Increase selectivity
	Co	Activate catalyst
	Ni	Reduce formation of coke
Ru	Y_2O_3	Increase efficiency of the catalyst

Table 9
Production of propanediol with different catalysts under different synthesis conditions.

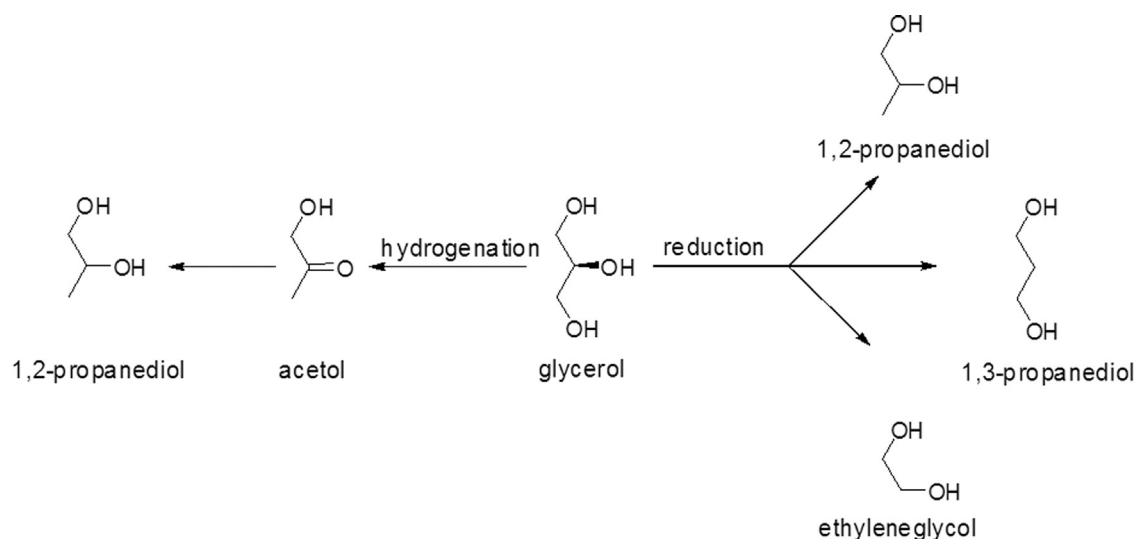| Reaction	Condition		References
	Temperature (°C)	Pressure (MPa)	
Zinc and copper catalyst along with sulfided Ru catalyst	240–270	15	[67]
Raney Cu, Cu–Pt, Cu–Ru and Cu/C	220–240	1–4	[68]
Cu, Co, Mo, Mn and an inorganic polyacid	259	25	[69]
Homogeneous catalyst containing W and group VII transition metal	200	32	[70]

Fig. 7. Catalytic conversion of glycerol to ethylene glycerol, 1,2- and 1,3-propanediol.

Table 10
Parameters involved in the catalytic glycerol reduction.

Catalyst system	Process parameters		Glycerol conversion (%)	References
	Temperature (°C)	Pressure (bar)		
Ru/S	250	300	99.4	[78]
$CuCr_2O_4$	200	10	84.4	[79]
Cu/Zn	260	10	99.4	[80]

Table 11
Series on catalytic etherification process of glycerol with different heterogeneous catalysts.

Reaction	Heterogeneous catalyst	References
Etherification of glycerol with ethanol	Sulfonic acid	[81]
	Zeolites	[82]
	Grafted silicas	[83]
	Heteropolyacid	[84]
	Mesoporous MoO_3/ SiO_2	[85]
Etherification of glycerol with butanal	Zeolite	[86]
Etherification of glycerol with methyl acetate	Sulfonic acid	[87]
Etherification of glycerol with aqueous formaldehyde	Amberlyst 15	[88]
	Zeolites	[89]
	P-toluenesulfonic acid	[90]

effectively achieved by the presence of heterogeneous catalyst (Table 11; Fig. 8).

The etherification process of glycerol showed the highest catalytic activity with sulfonic acid ($CH-SO_3H$) catalyst, due to the presence of sulfonic groups [80]. Ethers are simply generated from glycerol via treatment with isobutylene in the presence of an acid catalyst [81]. Glycerol's etherification with isobutylene was extensively investigated over sulfonic mesostructured silicas, strong acid ion-exchange resins, and zeolite, which resulted in the complete conversion of glycerol with 90% selectivity. Moreover, the incorporation of homogeneous catalysts, such as sodium, potassium, or carbonate hydroxide, produces polyglycerols with a mixture of lineal and cyclic characteristics. Positive effect on polyglycerol selectivity was reported with alkaline exchange zeolite catalysts. It is worth evaluating robust acid ion exchange resins as an appropriate catalyst for the production of commercial ethers from glycerol. The total yield of the etherification process can be improved via a two-phase reaction system involving a glycerol-rich polar phase (containing the acidic catalyst) and another phase consisting of an olefin-rich hydrocarbon phase where the product ethers can be readily separated.

Once acid catalyst is applied, the selectivity of the etherification process of glycerol becomes uncontrollable, with a mixture of di- to hexa-glycerol (lineal or cyclic) obtained, and consequently, produces a series of byproducts (polyglycerol ester and acrolein) [80]. Some studies modified the pseudo-pore size in these mesoporous materials to achieve better selectivity in the first-step reaction. Glycerol conversion was improved by the incorporation of Na_2CO_3 catalyst, resulting in low selectivity of di- and tri-glycerols. The impregnation of inorganic elements (e.g.: Al, Mg and La) into mesoporous catalysts is expected to modify both the selectivity of glycerol conversion, and hold the reaction constant. La and Mg demonstrated the most active and selective results. Furthermore, glycerol was converted into branched oxygen-containing components by catalytic etherification with either alkenes (isobutene) or alcohols (methanol or ethanol). The glycerol's etherification with tert-butanol occurred at 90 °C within 180 min in the presence of catex Amberlyst 15 catalyst and 96% conversion [82]. Works were done on glycerol etherification, with isobutene and tert-butanol without solvent, and it was discovered that isobutane demonstrated better conversion over different temperature ranges. The application of isobutane with macroreticular ion-exchange and/or sulfonic mesostructured silica catalyst indicated a 100% conversion of glycerol.

9. Catalytic ammoxidation glycerol

Direct production of acrylonitrile via ammoxidation of glycerol with mono- and mixed-oxides (e.g.: Mo, Bi, Sb, V, Sn, W, Zr, Ti, Ni, Al, P, G and Nb) catalyst is described in the literature review (Fig. 9). The catalysts have to be carefully selected to avoid the acidic centers of the catalyst from being blocked by ammonia via the reaction time. The ammonia/glycerol mol ratio varied between 1 and 1.5 at O_2:glycerol ratio of 0.5 and 10 respectively. The total conversion rate
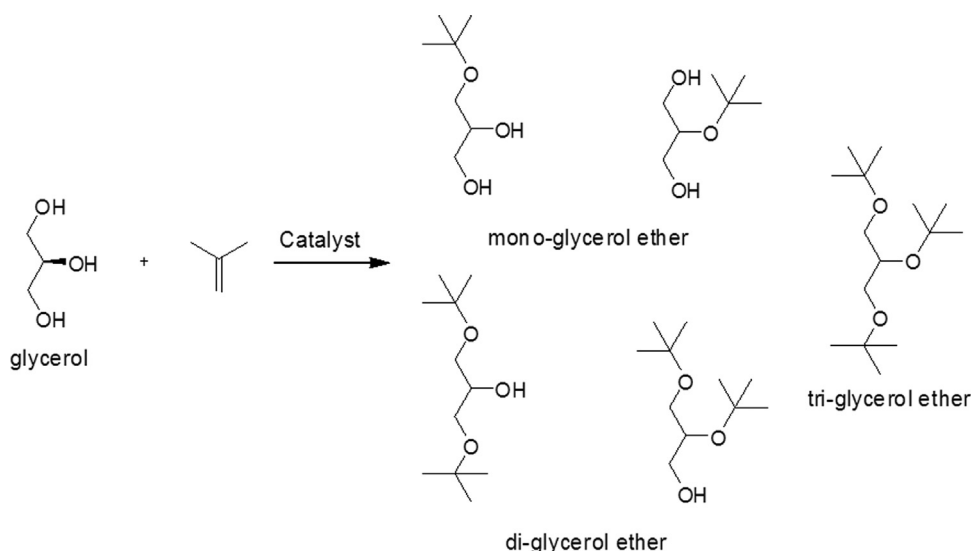
Fig. 8. Main reaction products in the etherification of glycerol.

is 100%, with a selectivity of 48% [83]. The injection of pure glycerol (10 wt% concentration) at 280 °C and 550 °C suggested the production of a direct ammoxidation process. Some studies used alumina-supported catalyst containing V, Sb, and Ni in a continuous fixed bed reactor [84]. Nb and Sb oxides supported on Al_2O_3 are extremely less reactive than the V-containing catalyst. Al_2O_3/Sb exhibits significant susceptibility to nitrile products (cetonitrile), while Al_2O_3/V is the most active, but produces acrolein, propanal, 1,2-propanediol, and cracking products. Al_2O_3/Sb and Al_2O_3/Ni oxide catalysts are relatively inactive, but both types of catalysts produce acrolein, and most interestingly, Al_2O_3/Sb exhibits a capacity to form C–N bonds [85]. However, these catalytic processes produced CO_2 as a subproduct to a yield of more than 50%. Thus, the indirect route was applied, allowing the independent choice of the catalyst and reaction parameters. The indirect route took into account the compatibility of the catalyst and conditions. Acid catalyst applied on the first step of dehydration might cause problems, considering the presence of NH_3, consequently blocking the catalysts' active side. Most of the ammoxidation process requires high processing temperature (first step: 270–300 °C; second step: 400–500 °C) [85]. Indirect ammoxidation involved two continuous steps: dehydration of glycerol, followed by ammoxidation of acrolein. Acid based catalysts are commonly used for the first step of dehydration. WO_3/TiO_2 system proved to be efficient for the glycerol's dehydration to acrolein and limited the production of sub-products (acetic acid, acetaldehyde and hydroxyacetone), with a yield of up to 70% acrolein. The challenges of reactions are more predominant in the second step of reaction with regards to large amount of impurities/subproducts from the first step of glycerol dehydration [86]. Some mixed oxides bases (e.g.: V/Al, VSb/Al and VSbNb/Al, Sb/Fe, Sn/Sb/Fe/O and Sb/Vd) are known for acrolein ammoxidation even in H_2O, and it was discovered that the conversion rate of acrolein increased by almost 6 times, and selectivity towards acrylonitrile was significantly improved. The results were more significant for the Sb/VO catalyst. At a ratios of 0.6 and 1.8 Sb/FeO catalyst, catalytic performance in acrolein ammoxidation was more favorable, with 44% selectivity and 81% conversion. XRD studies revealed that the addition of $FeSbO_4$ is correlated to the enhanced selectivity [87], due to the increment of catalyst surface and the formation of the $FeSbO_4$ phase. However, the reduction phase of Fe_2O_3 to Fe_3O_4 is possible once the reaction reached 400 °C [88]. Ammonia and O_2 content should be controlled to avoid the destruction of the desirable $FeSbO_4$ phase. Feeding ammonia during the reaction of glycerol drives the production distribution towards
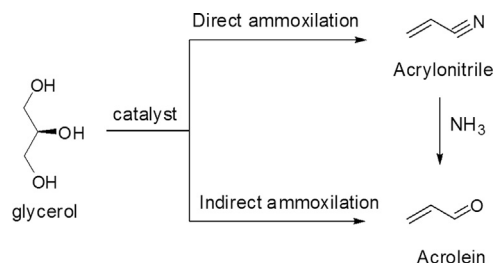

Fig. 9. Direct and indirect glycerol conversions via ammoxidation process.

nitriles. Acrylonitrile production dropped by 10% with the increase of the NH_3:acrolein ratio, caused by the deactivation of dehydration catalyst, resulting in the reduction of acrolein concentration [84].

10. Catalytic acetalization of glycerol

Through the acetalization process, glycerol reacts with simple C=O compounds to provide isomeric six-(1,3-dioxane) and five-membered (1,3-dioxolane) cyclic products as novel fine chemical intermediates [89]. However, there is no such ratio of 50:50 on the production of each 1,3-dioxane and 1,3-dioxolane being reported, and research was encouraged on varying the reaction parameters, including the molar ratio of carbonyl compound to glycerol and temperature to modify the selectivity of the reaction [89]. However, none of the related approaches reported a complete conversion of glycerol acetalization, with no isomeric six-(1,3-dioxane) being produced. In addition, complete selectivity towards solketal and acetal for both isomerix 6 and 5 did not manage to reach supercritical conditions (with hazardous dichloromethane solvent) [90]. The complete isomerix six (1,3-dioxane) produced with the aldehydes was facilitated at the evaluated temperature, and this reaction is not regarded as being environmentally-friendly. Thus, researchers used homogeneous acid catalyst (e.g.: HCl, divinylbenzene–styrene resin, H_3PO_4, and p-toluenesulfonic acid (PTSA)) for glycerol acetalization [91]. Efforts were made to use heterogeneous catalyst for glycerol acetalization with ketones and/or aldehyde to control the selectivity in glycerol solketal and acetal production. Indeed, heterogeneous catalyst is easily separated from the reaction mixture, either by filtration or by centrifugation, and do not require neutralization. The catalytic glycerol acetalization with ketones

is reported quite frequently, and yield the five-membered (1,3-dioxolane) cyclic only. Furthermore, the use of organic solvents (e.g.: chloroform, benzene and toluene) improved the glycerol conversion rates. This route is regarded as effective, inexpensive, and more reliable in terms of acetalization of glycerol. For example, glycerol has been selectively converted to branched oxygenated compounds of five and six-membered (1,3-dioxolane) through solventless acetalization process, with acetone catalyzed by mesoporous 5% Ni–1% Zr supported activated carbon catalyst. The reaction was performed with only 0.20 g of catalyst, N_2-flow at 45 °C [91]. The chromatography showed a complete conversion process, with selectivities of 26% and 74% in five and six-membered (1,3-dioxolane), respectively. The catalytic activity attributed to the intercalated NiO and ZrO_2 species into the activated carbon structure and the surface characteristics. Solid acid catalysts, including MoOx or Wox, promoted ZrO_2 catalyst for use in catalyzing the glycerol acetalization, due to the nature of its active sites, which are defined either by the presence of surface proteins (Bronsted acid sites), or by coordinating unsaturated cationic centers (Lewis acid sites). This catalyst is environmentally benign, easy to prepare, owning a better thermal stability, and display strong surface acidity, making it a promising candidate [92]. The use of zirconia-based mixed oxides and subsequent impregnation with molybdate ions are efficient ways of enhancing catalytic performance. Mixed oxides show superior physicochemical and acidic properties than mono-oxides, resulting in superior catalytic activity. MoO_3 promoted zirconia-based metal oxide catalyst, currently receiving attention with the catalyzed acetalization of glycerol with different kinds of benzaldehydes under solvent free conditions. ZrO_2 and TiO_2–ZrO_2, and the respective MoO_3 promoted catalyst were prepared by a facile precipitation and wet-impregnation method, and it was discovered that almost 74% glycerol conversion observed by 51% is selected on 1,3-dioxane production. However, the conversion of glycerol relatively decreased with substituted benzaldehydes, due to the presence of stearic hindrance structure [90]. Similar observation occurred in the case of p-anisaldehyde with $MoOx/TiO_2$–ZrO_2 solid acid catalyst, where up to 71% of the selectivity of 1,3-dioaxane is obtained. The potential of MoO_3-supported SiO_2 and Al_2O_3 is being extensively investigated due to its catalytic activity in oxidation and organic reactions. Acetalization of glycerol with benzaldehyde was carried out using a series of MoO_3/SiO_2 catalyst, with varied MoO_3 loading (1–2 mol%). 20 mol% of MoO_3/SiO_2 catalyst is the most active catalyst in acetalization under mild conditions. Glycerol conversion reached 72% with 60% selectivity on a six-membered acetal, thus encouraging the use of a number of solid acids in the acetalization process (e.g.: protic acid, Lewis acid (ZnCl), alumina, montmorillonite, zeolite, mesoporous alumina-silicates) and ion exchange resins [92].

11. Conclusion and further research

Current review highlights many possible processes for the catalytic conversion of glycerol into useful chemicals. The purification of glycerol is a high-value commercial product, with wide range of applications. Scientists devised ways to deconstruct different chemical platforms derived from glycerol with regards to simpler and more understood chemistries, designed to provide various end-products. Being a polyol with 3 hydroxyl groups with different reactivities, multiple chemistries, ranging from redox (oxidations and hydrogenolysis) to acid-catalyzed processes (etherifications, esterification), dehydrations and oligomerisatons were designed and optimized. In most of the related studies, it is still difficult to obtain good selectivity in the desired products at high glycerol conversion due to the wide hydroxylic functionalization of

the triol glycerol molecule of similar reactivity, and owing to unknown reaction conditions or the lack of optimal catalysts. Chemically, glycerol is catalytically transformed to oxidation products on metallic catalysts using promoter glycols via hydrogenolysis on Ru, Cu and Pt catalysts, polyglycerols by etherification on zeolites and mesoporous materials and syngas by pyrolysis and gasification. However, significant challenges still need to be addressed in terms of developing chemical platforms under aqueous processing conditions, design of stable and active catalysts, and essentially different processing techniques for glycerol. In the future, new heterogeneous catalysts stable under the reaction conditions are extremely desirable. However, the enhancement of the economic value added products viability industry through new applications of crude glycerol is still under investigation. In addition, a heterogeneous catalyzed process to obtain a higher quality of glycerol is an appropriate alternative. This will demonstrate a better possibility by catalytic convertion process to energy and value-added chemicals and preferably, will offer a more economically viable biofuel producers.

Acknowledgment

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